Visible-light-induced C-H Annulation by Metal-decorated Covalent Organic Frameworks with Fe-bipyridyl linkages

Chen Zhang *

Soochow University, suzhou, jiangsu, China

* Corresponding Author Email: 1815709167@qq.com

Abstract. The integration of transition metal and photoredox catalyst achieves a harmonious cooperation between sophisticated chemical transformations and judicious utilization of light energy. The previous work was exclusively accomplished through employment of homogeneous transition-metal catalysts or photoredox catalysts. In this study, we present the synthesis of iron-decorated covalent organic frameworks (Fe-COF) and its application on C-H annulation of amides with alkynes by irradiation of visible light. The iron center prompts robust chelation with amides, leading to C-H activation, subsequently. Meanwhile, the photoactive covalent organic framework facilitates visible light absorption and accelerates the C-H activation step. Significantly, isoquinolin-1(2H)-one derivatives with high yield and selectivity were obtained in the presence of Fe-COF under visible light, and highlighting the covalent organic framework's stability and inherent heterogeneous property with repeatable chemical recyclability.

Keywords: iron-decorated covalent organic frameworks (Fe-COF), Organic catalysis, C-H annulation.

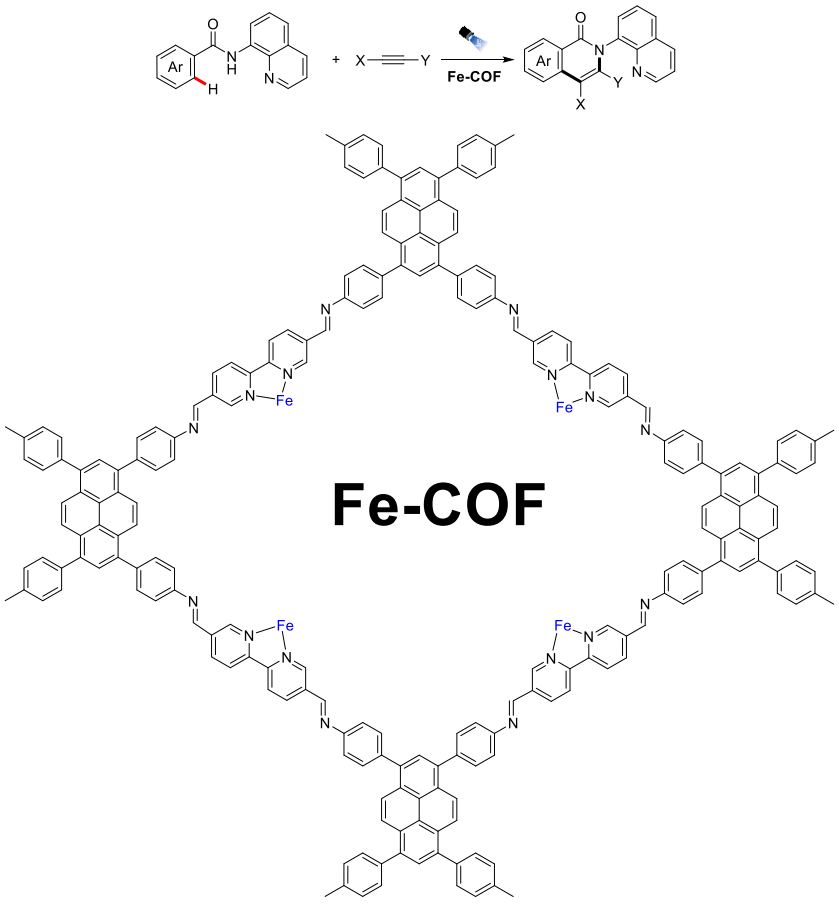
1. Introduction

The past decades have witnessed a remarkable resurgence in photocatalyzed organic transformations that promoted by organic photosensitizer under visible light [1]. With the help of photoredox catalyst, the visible-light-driven organic transformations could be proceeded more environmentally friendly by avoiding use of the most common environmental health hazards ultraviolet light [2]. As we know, the radicals are the highly reactive intermediates in photoredox catalysis, which is induced by single electron transfer (SET) [3], hydrogen atom transfer (HAT) [4], proton-coupled electron transfer (PCET) [5], or energy transfer processes [6]. However, the problem of chemo-, regio-, and stereo selectivity were rarely addressed in photocatalyzed organic reactions and facing challenges are still enormous [7]. Gratifyingly, metallaphotoredox catalysis, the merger of photoredox and transition metal catalysis, offers a convenient and broadly applicable strategy to address the above issue. Based on this, metallaphotoredox-mediated process to form C-C, C-N, C-O, or C-S bonds by cross coulping with aryl halogens or leaving groups [8]. Furthermore, C-H activation, the Holy Grail of modern Chemistry, remains a long-term assignment in modern synthetic chemistry. Visible-light-induced C-H activation via radical reaction pathways has been a hot topic and attracted extensive exploration over the past decade [9]. However, most schemes adopt strategy needs to add homogeneous catalyst, which is unrecoverable and causing metallic residues. Therefore, to promote the development of large-scale industrial sustainability through green chemistry, transition-metal-decorated hetergenerous photocatalysts may address these shorcomings by incorporating metal ions into COF skeleton.

Covalent organic frameworks (COF) are a novel class of crystalline organic porous materials constructed by covalently linked molecular building blocks [10]. With the advantages of low density, large specific surface area, high stability and good designability, COF have shown potential applications in the fields of adsorption, separation, catalysis, energy storage, sensing, and membrane materials [11]. As a kind of crystalline organic porous materials, COF have been widely studied in catalytic applications because they can provide adjustable catalytic sites. Recently, metal-decorated COF (M-COF) as a bridge by integrating homogeneous metal ions into photoactive hetergeneous COF have emerged [12]. It opens up opportunities for designing desirable organic frameworks with

adjustable structures and functionality for organic catalysis. However, only a limited variety of M-COF have been reported to date. For example, some groups developed some Ni or Ni/Ir- COF, which further promoted C-C, C-O, or C-S cross-couplings from aryl halogen under visible light [13]. This strategy has particular advantages of combining transition metal's catalytic activity and COF's large π-conjugated systems photo reactivities. In the recent years, cobalt-catalyzed C–H activation has emerged as a powerful tool for sustainable syntheses and notable success was achieved using cobalt-complexes under mild reaction conditions. For example, Jiang and coworkers developed a facile strategy to the manipulation of the cobalt spin state by changing the oxidation state of cobalt in the porphyrin over covalent organic frameworks, which exhibits favorable activity and significantly enhanced selectivity from CO_2 to HCOOH rather rather than CO and CH_4[14].

Herein, we report the synthesis of Fe-COF and its photocatalytic performance on C-H bond annulation of amides with alkynes. In this catalytic process, Fe-COF fulfills metal chalation, C-H activation, cyclization of acetylene by irradiation of visible light. This means two birds with one stone. Moreover, reusability of Fe-COF is important for green chemistry and industrial application.



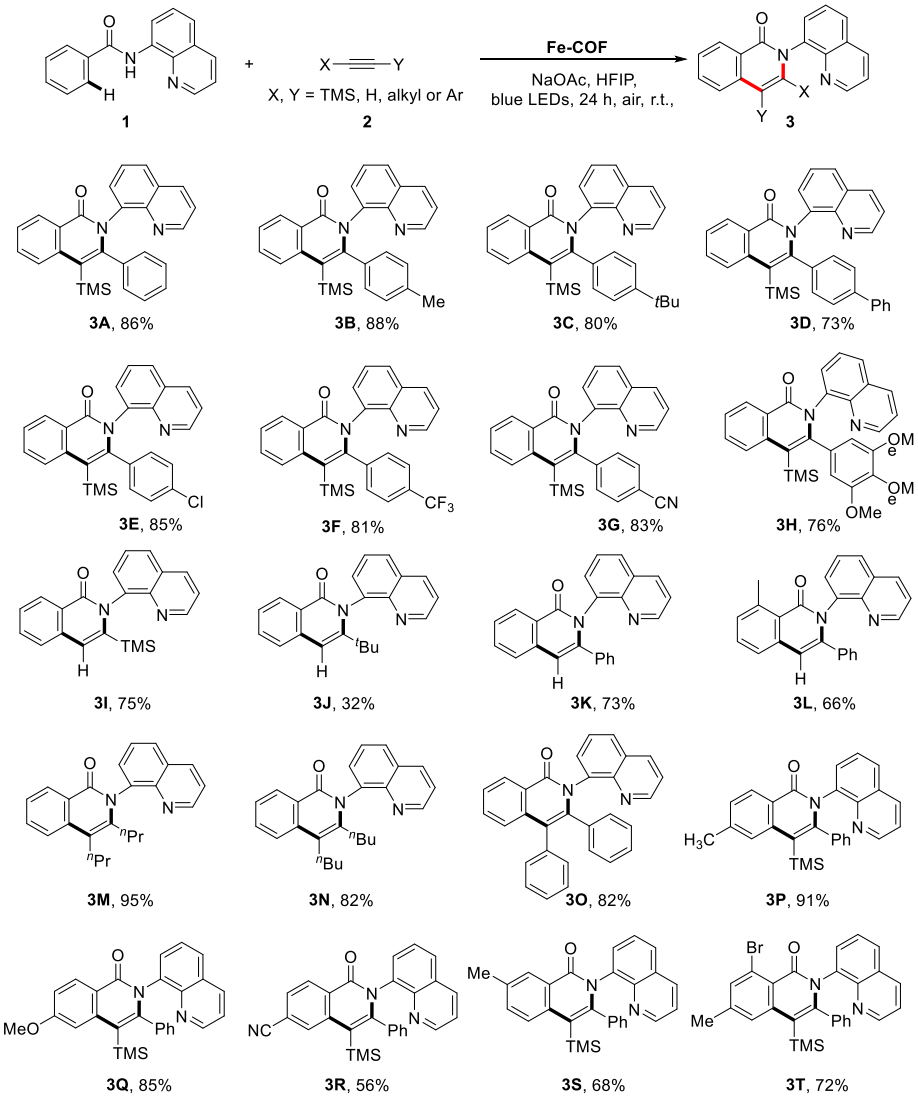
Scheme 1. Fe-COF catalyzed C-H Annulation of Amides with Alkynes under visible light.

2. Results and Discussion

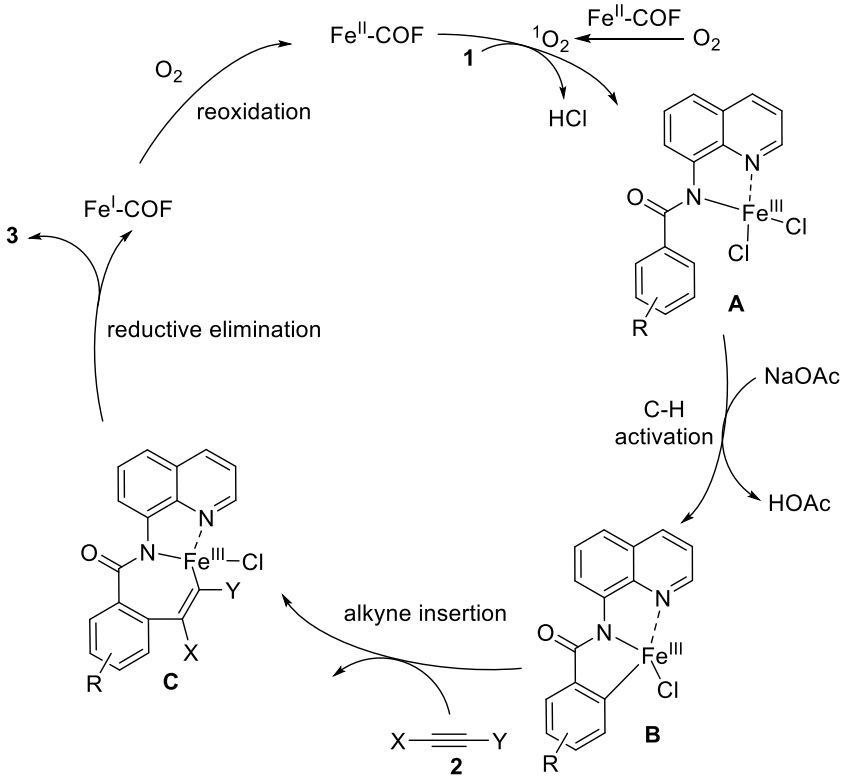
Crystalline COF was synthesized by condensation of commercially available compounds [2,2'-bipyridine]-5,5'-dicarbaldehyde and 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetraaniline with the assistance of acetic acid aqueous solution in the presence of mesitylene and dioxane solution at 120 °C for 3 days by solvothermal method. The light yellow crystalline powder was obtained and washed with acetone and THF in turn, then the resulted samples was dried under vacuum at 60 °C overnight. What needs to be pointed out is that the synthetic precedure was referring to previous reported work. From a synthetic perspective, dipyridyl unit is important coordinated site, where transition metal could be introducted to bond to dipyridyl building block. Herein, we reported our strategy for construction of

Fe-COF, which could be easily accessed by refluxing of COF with Iron(II) chloride in CH_3CN solvent. Dark red Fe-COF was obtained in almost quantitative yield.

With the Fe-COF material in hand, we next explored its catalytic property on the C-H annulation of amides and alkynes. To our delight, the desired product **3**, starting from various amides and alkynes could be obtained in favourable yields under visible light irradiation in the air at room temperature. The reaction was performed using Fe-COF as photocatalyst, 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) as solvent, NaOAc as base, air as oxidant, and blue LEDs as light source. As shown in Scheme 2, regarding the trimethyl(arylethynyl)silane partner, a wide range of typical substituents were found to be compatible in this transformation, and products **3A-3H** were obtained in 73-88% yields. To our delight, monosubstituted alkynes were also suitable to this transformation, affording the corresponding product **3I-3L** in acceptable yields (32-75%). In addition, symmetrical diacetylene, including oct-4-yne, dec-5-yne, 1,2-diphenylethyne were also tolerated and provided the expected product **3M-3O** in good yields. Remarkly, a range of substituents at different position on amide derivative proceeded smoothly, delivering the desired product **3P-3T** in a moderate to excellent yields. The above results indicated that this catalytic system is compatible with various of amides and alkynes.



Scheme 2. Substrate scope for the visible light-mediated Fe-COF-catalyzed C-H annulation of amides and alkynes.



Scheme 3. Proposed mechanism for the visible light-mediated Fe-COF-catalyzed C-H annulation of amides and alkynes.

On the basis of the obtained results, a plausible mechanism for the Fe-COF-catalyzed C-H annulation of amides with alkynes was proposed in Scheme 3. First, the occurrence of singlet oxygen $^1O_2$ is an important driving force of this reaction, followed by oxidation of Fe(II) to Fe(III) by singlet oxygen via energy transfer that leads to the generation of the intermediate **A** . Next, intermediate **B** was formed through C-H activation in the prence of NaOAc as base. Then, alkyne was trapped by the intermediate **B** to furnish the intermediate **C**. Finally, reductive elimination of intermediate **C** leads to the formation of product **3** by releasing the Fe(I)-COF species, which could be reoxidized to Fe(II)-COF photocatalyst by single oxygen.

3. Conclusion

In summary, we have developed a visible light-mediated Fe-COF-catalyzed C-H annulation between amides and alkynes, providing a new approach to access isoquinolin-1(2H)-one derivatives. This protocol allows Fe-COF to perform C-H activation, alkyne insertion, and subsequent releasing Fe-COF catalyst to achieve catalytic cycle. This catalytic system established a platform and encouraged us to develop further application of Fe-COF on other visible-light-driven organic reactions.

4. Experimental Section

1 (0.1 mmol), Fe-COF (5 mg), NaOAc•3H_2O (1 equiv.), **2** (0.15 mmol) and HIFP (2 mL) were added to a glass tube. The mixture was stirred under air with the blue light irradiation (456 nm) for 24 h at room temperature. Upon completion, the Fe-COF was filtered while the solvent was concentrated under the reduced pressure. The residue was then purified by flash chromatography on silica gel to afford the desired product **3**.

3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3A)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91 (dd, *J* = 4.2 Hz, *J* = 1.6 Hz, 1H), 8.58-8.56 (m, 1H), 8.04-8.00 (m, 2H), 7.73-7.69 (m, 1H), 7.62 (dd, *J* = 7.0, 2.6 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.36-7.30

(m, 3H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 6.62 (t, *J* = 7.6 Hz, 1H), 0.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 150.7, 149.5, 144.9, 140.6, 137.8, 137.4, 136.0, 131.7, 131.3, 131.1, 130.1, 128.9, 128.7, 128.4, 128.3, 127.6, 126.9, 126.6, 126.1, 126.1, 125.7, 121.5, 111.5, 2.2. HRMS (ESI) [M+H]+ m/z calcd for $C_{27}H_{25}N_2OSi$ 421.1720, found 421.1731.

2-(quinolin-8-yl)-3-(p-tolyl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3B)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.1 Hz, *J* = 1.5 Hz, 1H), 8.55-8.53 (m, 1H), 8.04 (dd, *J* = 8.3 Hz, *J* = 1.5 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.71-7.68 (m, 1H), 7.63 (dd, *J* = 7.3 Hz, *J* = 2.3 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.36-7.30 (m, 3H), 7.05 (dd, *J* = 7.8 Hz, *J* = 1.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.70 (dd, *J* = 7.9 Hz, *J* = 1.6 Hz, 1H), 6.42 (d, *J* = 7.8 Hz , 1H), 2.08 (s, 3H), 0.00 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 150.8, 149.8, 145.1, 140.8, 138.0, 136.0, 134.7, 131.7, 131.3, 131.0, 130.0, 128.9, 128.7, 128.4, 127.6, 127.6, 127.4, 126.2, 126.0, 125.8, 121.5, 111.7, 21.2, 2.3. HRMS (ESI) [M+H]+ m/z calcd for $C_{28}H_{27}N_2OSi$ 435.1874, found 435.1887.

3-(4-(tert-butyl)phenyl)-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3C)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91 (dd, *J* = 4.2 Hz, *J* = 1.6 Hz, 1H), 8.55 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1H), 8.05-7.98 (m, 2H), 7.72-7.68 (m, 1H), 7.60 (t, *J* = 4.8 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.37-7.33 (m, 1H), 7.30 (d, *J* = 4.8 Hz, 2H), 7.05 (s, 2H), 6.70 (d, *J* = 8.3 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 1.07 (s, 9H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 151.5, 150.6, 149.8, 144.9, 140.7, 137.9, 136.1, 134.5, 131.7, 131.1, 131.0, 129.8, 128.9, 128.7, 128.2, 127.6, 126.2, 126.0, 125.8, 123.6, 123.4, 121.4, 111.6, 34.4, 31.1, 2.2. HRMS (ESI) [M+H]+ m/z calcd for $C_{31}H_{33}N_2OSi$ 477.2368, found 477.2357.

3-([1,1'-biphenyl]-4-yl)-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3D)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 4.1 Hz, *J* = 1.5 Hz, 1H), 8.53-8.51 (m, 1H), 7.99- 7.95 (m, 2H), 7.68-7.65 (m, 1H), 7.57-7.55 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.34-7.30 (m, 4H), 7.30-7.26 (m, 4H), 7.22 (d, *J* = 7.1 Hz, 1H), 7.20-7.18 (m, 1H), 6.88-6.83 (m, 2H), 0.00 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 150.8, 149.3, 145.0, 140.7, 140.7, 140.1, 137.9, 136.5, 136.1, 131.8, 131.7, 131.1, 130.6, 128.9, 128.8, 128.8, 128.6, 127.7, 127.6, 126.9, 126.2, 126.2, 125.8, 125.4, 125.2, 121.5, 111.8, 2.4. HRMS (ESI) [M+H]+ m/z calcd for $C_{33}H_{29}N_2OSi$ 497.2029, found 497.2029.

3-(4-chlorophenyl)-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3E)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 4.1 Hz, *J* = 1.4 Hz, 1H), 8.55 (d, *J* = 7.9 Hz, 1H), 8.06 (dd, *J* = 8.3 Hz, *J* = 1.3 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.73-7.66 (m, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.35 (q, *J* = 4.0 Hz, 3H), 7.12 (dd, *J* = 8.2 Hz, *J* = 2.0 Hz, 1H), 7.04 (dd, *J* = 8.2 Hz, *J* = 2.0 Hz, 1H), 6.84 (dd, *J* = 8.3 Hz, *J* = 2.0 Hz, 1H), 6.63 (dd, *J* = 8.3 Hz, *J* = 2.0 Hz, 1H), 0.03 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 150.8, 148.1, 144.8, 140.4, 137.6, 136.2, 136.0, 134.3, 132.6, 131.8, 131.5, 131.1, 128.9, 128.8, 128.8, 127.7, 127.2, 126.9, 126.4, 126.3, 125.8, 121.6, 111.9, 2.4. HRMS (ESI) [M+Na]+ m/z calcd for $C_{27}H_{23}ClN_2OSiNa$ 477.1165, found 477.1165.

2-(quinolin-8-yl)-3-(4-(trifluoromethyl)phenyl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3F)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.2 Hz, *J* = 1.6 Hz, 1H), 8.58-8.55 (m, 1H), 8.06-8.00 (m, 2H), 7.75-7.71 (m, 1H), 7.65 (dd, *J* = 7.3 Hz, *J* = 2.3 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.38-7.32 (m, 5H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 0.00 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9, 150.9, 147.8, 144.8, 140.9 (q, *J* = 1.2 Hz), 140.3, 137.4, 136.2, 131.9, 131.7, 131.1, 130.7, 130.4 (q, *J* = 32.7 Hz), 129.0, 128.9, 128.8, 127.7, 126.6, 126.3, 125.8, 123.9 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.2 Hz), 123.5 (q, *J* = 3.7 Hz), 121.7, 111.9, 2.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.85. HRMS (ESI) [M+Na]+ m/z calcd for $C_{28}H_{23}F_3N_2OSiNa$ 511.1129, found 511.1427.

4-(1-oxo-2-(quinolin-8-yl)-4-(trimethylsilyl)-1,2-dihydroisoquinolin-3-yl)benzonitrile (3G)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (d, *J* = 2.8 Hz, 1H), 8.55 (d, *J* = 7.7 Hz, 1H), 8.06 (d, *J* = 7.3 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.75-7.67 (m, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.39-7.29 (m, 5H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 0.00 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 151.0, 147.1, 144.6, 141.8, 140.2, 137.2, 136.3, 132.0, 131.2, 131.1, 130.7, 130.4, 129.2, 129.0, 128.9, 127.7, 126.8, 126.3, 125.9, 121.8, 118.3, 112.1, 112.0, 2.3. HRMS (ESI) [M+H]+ m/z calcd for $C_{28}H_{24}N_3OSi$ 446.1701, found 446.1683.

2-(quinolin-8-yl)-3-(3,4,5-trimethoxyphenyl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3H)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (dd, *J* = 4.1 Hz, *J* = 1.5 Hz, 1H), 8.55-8.52 (m, 1H), 8.10 (dd, *J* = 8.3 Hz, *J* = 1.4 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.72-7.66 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.39 (dd, *J* = 8.3 Hz, *J* = 4.2 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.28-7.26 (m, 1H), 6.45 (d, *J* = 1.6 Hz, 1H), 6.08 (d, *J* = 1.5 Hz, 1H), 3.77 (s, 3H), 3.63 (s, 3H), 2.96 (s, 3H), 0.08 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 152.1, 151.7, 150.7, 149.2, 145.5, 140.6, 138.3, 138.0, 136.4, 132.8, 131.8, 130.5, 128.9, 128.8, 128.7, 127.6, 126.3, 126.2, 126.1, 121.4, 111.5, 109.2, 108.2, 61.0, 56.4, 55.4, 2.3. HRMS (ESI) [M+H]+ m/z calcd for $C_{30}H_{31}N_2OSi$ 511.2071, found 511.2048.

(quinolin-8-yl)-3-(trimethylsilyl)isoquinolin-1(2H)-one (3I)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (d, *J* = 4.1 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.73-7.65 (m, 3H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.51 (t, *J* J = 7.5 Hz, 1H), 7.41 (dd, *J* = 7.6 Hz, *J* = 3.5 Hz, 1H), 6.91 (s, 1H), -0.26 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 151.4, 146.8, 145.5, 139.4, 137.0, 136.2, 132.4, 130.5, 129.6, 129.3, 128.1, 127.4, 126.5, 126.3, 126.0, 121.9, 115.5, 0.0. HRMS (ESI) [M+H]+ m/z calcd for $C_{21}H_{21}N_2OSi$ 345.1409, found 345.1418.

3-(tert-butyl)-2-(quinolin-8-yl)isoquinolin-1(2H)-one (3J)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.0 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 7.3 Hz, 1H), 7.68-7.63 (m, 2H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.37 (dd, *J* = 8.1 Hz, *J* = 4.1 Hz, 1H), 6.81 (s, 1H), 1.05 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 151.6, 151.1, 146.4, 139.2, 137.4, 136.2, 132.6, 131.9, 129.4, 129.1, 128.1, 126.5, 126.3, 125.7, 124.7, 121.7, 104.5, 36.7, 31.3. HR-MS (ESI) [M+H]+ m/z calcd for $C_{22}H_{21}N_2O$ 329.1639, found 329.1648.

3-phenyl-2-(quinolin-8-yl)isoquinolin-1(2H)-one (3K)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91-8.90 (m, 1H), 8.50 (d, J = 8.0 Hz, 1H), 8.08-8.06 (m, 1H), 7.70 (t, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.35 (dd, *J* = 8.3 Hz, *J* = 4.2 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 2H), 6.66 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 151.0, 144.8, 144.6, 137.4, 137.3, 136.4, 136.1, 132.8, 130.8, 128.8, 128.8, 128.5, 128.0, 127.4, 126.8, 126.2, 125.9, 125.5, 121.6, 107.5. HRMS (ESI) [M+H]+ m/z calcd for $C_{24}H_{17}N_2O$ 349.1326, found 349.1335.

8-methyl-3-phenyl-2-(quinolin-8-yl)isoquinolin-1(2H)-one (3L)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92-8.91 (m, 1H), 8.08-8.05 (m, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.55-7.51 (m, 2H), 7.43 (m, 2H), 7.35 (dd, *J* = 8.3 Hz, *J* = 4.2 Hz, 1H), 7.27-7.25 (m, 1H), 7.12 (d, J = 7.2 Hz, 2H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.94 (t, *J* = 7.3 Hz, 2H), 6.60 (s, 1H), 2.92 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 151.0, 144.9, 144.3, 142.5, 139.1, 137.8, 136.4, 136.2, 132.0, 131.0, 129.9, 128.9, 128.8, 128.6, 127.9, 127.3, 126.0, 124.7, 124.0, 121.6, 107.9, 24.0. HRMS (ESI) [M+H]+ m/z calcd for $C_{25}H_{19}N_2O$ 363.1487, found 363.1492.**2-**

3,4-dipropyl-2-(quinolin-8-yl)isoquinolin-1(2H)-one (3M)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 4.1 Hz, *J* = 1.5 Hz, 1H), 8.47 (d, *J* = 7.8 Hz, 1H), 8.23 (dd, *J* = 8.3 Hz, *J* = 1.4 Hz, 1H), 7.95 (dd, *J* = 7.9 Hz, *J* = 1.4 Hz, 1H), 7.76-7.65 (m, 4H), 7.46-7.40 (m, 2H), 2.82-2.73 (m, 2H), 2.53-2.45 (m, 1H), 1.98-1.91 (m, 1H), 1.79-1.69 (m, 2H), 1.43-1.26 (m, 2H), 1.12 (t, *J* = 7.3 Hz, 3H), 0.54 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 151.4, 144.9, 141.1, 137.7, 137.6, 136.3, 132.4, 130.4, 129.3, 129.1, 128.8, 126.2, 125.7, 125.6, 123.0, 121.8, 113.6, 32.9, 30.0, 23.8, 23.1, 14.6, 14.3. HRMS (ESI) [M+H]+ m/z calcd for $C_{24}H_{25}N_2O$ 357.1952, found 357.1961.

3,4-dibutyl-2-(quinolin-8-yl)isoquinolin-1(2H)-one (3N)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (dd, *J* = 4.1 Hz, *J* = 1.6 Hz, 1H), 8.47 (d, *J* = 7.4 Hz, 1H), 8.22 (dd, *J* = 8.3 Hz, *J* = 1.5 Hz, 1H), 7.95 (dd, *J* = 7.9 Hz, *J* = 1.5 Hz, 1H), 7.76-7.67 (m, 4H), 7.46-7.40 (m, 2H), 2.86-2.74 (m, 2H), 2.52-2.45 (m, 1H), 2.05-1.96 (m, 1H), 1.76-1.64 (m, 2H), 1.59-1.50 (m, 2H), 1.41-1.22 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.96-0.87 (m, 2H), 0.49 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 151.4, 145.0, 141.0, 137.7, 137.6, 136.3, 132.4, 130.4, 129.4, 129.1, 128.8, 126.2,

125.6, 125.6, 122.9, 121.8, 113.7, 32.7, 31.5, 30.3, 27.6, 23.3, 22.6, 14.1, 13.2. HRMS (ESI) [M+H]+ m/z calcd for $C_{26}H_{29}N_2O$ 385.2266, found 385.2274.

3,4-diphenyl-2-(quinolin-8-yl)isoquinolin-1(2H)-one (3O)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94- 8.93 (m, 1H), 8.60 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.53 (dd, *J* = 13.3 Hz, *J* = 7.0 Hz, 2H), 7.40-7.35 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.26 (s, 2H), 7.19-7.16 (m, 3H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.78-6.71 (m, 2H), 6.50 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 150.9, 144.8, 142.0, 138.3, 137.8, 136.7, 136.1, 135.0, 132.5, 132.0, 131.8, 131.0, 130.9, 129.9, 128.8, 128.7, 128.5, 128.1, 127.9, 127.3, 126.9, 126.8, 126.7, 126.5, 125.8, 125.7, 125.7, 121.6, 118.6. HRMS (ESI) [M+H]+ m/z calcd for $C_{30}H_{21}N_2O$ 425.1647, found 425.1648.

6-methyl-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3P)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 4.1 Hz, *J* = 1.5 Hz, 1H), 8.48 (d, *J* = 8.1 Hz, 1H), 7.99 (dd, *J* = 8.3 Hz, *J* = 1.4 Hz, 1H), 7.81 (s, 1H), 7.59 (dd, *J* = 7.9 Hz, *J* = 1.3 Hz, 1H), 7.35-7.28 (m, 4H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.63 (t, *J* = 7.5 Hz, 1H), 2.56 (s, 3H), 0.03 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9, 150.6, 149.6, 144.9, 141.9, 140.7, 137.8, 137.4, 135.9, 131.3, 131.0, 130.0, 128.7, 128.6, 128.3, 128.1, 127.6, 127.5, 126.8, 126.5, 125.6, 123.8, 121.3, 111.1, 22.3, 2.2. HRMS (ESI) [M+H]+ m/z calcd for $C_{28}H_{27}N_2OSi$ 435.1873, found 435.1887.

6-methoxy-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3Q)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91 (dd, *J* = 4.2 Hz, *J* = 1.6 Hz, 1H), 8.48 (d, *J* = 8.9 Hz, 1H), 8.02 (dd, *J* = 8.3 Hz, *J* = 1.6 Hz, 1H), 7.61 (dd, *J* = 7.0, 2.5 Hz, 1H), 7.39 (d, *J* = 2.3 Hz, 1H), 7.35-7.29 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.09 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.62 (t, *J* = 7.6 Hz, 1H), 3.96 (s, 3H), 0.01 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 162.3, 150.8, 150.3, 145.0, 142.6, 137.9, 137.5, 136.0, 131.3, 131.2, 130.9, 130.1, 128.7, 128.4, 128.3, 127.0, 126.6, 125.7, 121.5, 120.0, 114.9, 110.9, 109.9, 55.5, 2.2. HR-MS (ESI) [M+H]+ m/z calcd for $C_{28}H_{27}N_2O_2Si$ 451.1827, found 451.1836.

1-oxo-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)-1,2-dihydroisoquinoline-6-carbonitrile (3R)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 4.1 Hz, *J* = 1.5 Hz, 1H), 8.62 (d, *J* = 8.2 Hz, 1H), 8.30 (s, 1H), 8.04 (dd, *J* = 8.3 Hz, *J* = 1.5 Hz, 1H), 7.69 (dd, *J* = 8.3 Hz, *J* = 1.2 Hz, 1H), 7.64 (t, *J* = 4.8 Hz, 1H), 7.36 (dd, *J* = 8.3 Hz, *J* = 4.2 Hz, 1H), 7.33 (d, *J* = 4.8 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.64 (t, *J* = 7.5 Hz, 1H), 0.01 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6, 151.2, 150.5, 144.2, 140.5, 136.8, 136.3, 135.8, 131.9, 130.7, 130.5, 129.7, 129.5, 128.5, 128.4, 127.5, 126.8, 126.5, 125.4, 121.4, 118.5, 114.9, 110.6, 1.7. HRMS (ESI) [M+H]+ m/z calcd for $C_{28}H_{24}N_3OSi$ 446.1671, found 446.1683.

7-methyl-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3S)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.2 Hz, *J* = 1.7 Hz, 1H), 8.00 (dd, *J* = 8.3 Hz, *J* = 1.6 Hz, 1H), 7.71 (s, 1H), 7.63 (s, 1H), 7.60-7.58 (m, 1H), 7.37-7.26 (m, 4H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.05- 7.01 (m, 1H), 6.93 (d, *J* = 14.9 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.63-6.59 (m, 1H), 2.48 (s, 3H), -0.03 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 150.7, 148.6, 145.0, 138.2, 138.0, 137.5, 136.0, 136.0, 133.2, 131.4, 131.1, 130.2, 128.7, 128.4, 128.4, 128.2, 127.6, 126.9, 126.6, 126.1, 125.7, 121.4, 111.3, 21.4, 2.2. HR-MS (ESI) [M+H]+ m/z calcd for $C_{28}H_{27}N_2OSi$ 435.1873, found 435.1887.

8-bromo-6-methyl-3-phenyl-2-(quinolin-8-yl)-4-(trimethylsilyl)isoquinolin-1(2H)-one (3T)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.2 Hz, *J* = 1.7 Hz, 1H), 8.00 (dd, *J* = 8.3 Hz, *J* = 1.6 Hz, 1H), 7.71 (s, 1H), 7.63-7.62 (m, 1H), 7.59 (dd, *J* = 7.9 Hz, *J* = 1.6 Hz, 1H), 7.37-7.29 (m, 3H),7.13 (d, *J* = 7.6 Hz, 1H), 7.05-7.01 (m, 1H), 6.93 (d, *J* = 14.9 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.64-6.59 (m, 1H), 2.48 (s, 3H), -0.03 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1, 150.7, 150.6, 144.9, 143.8, 141.8, 137.8, 137.2, 136.0, 134.7, 131.3, 131.2, 130.1, 128.8, 128.4, 128.4, 127.9, 127.0, 126.6, 125.7, 123.6, 121.5, 121.3, 110.8, 21.6, 2.3. HR-MS (ESI) [M+H]+ m/z calcd for $C_{28}H_{26}BrN_2OSi$ 513.0978, found 513.0992.

Acknowledgements

We gratefully acknowledge the supports from the National Natural Science Foundation of China (21976076).

References

[1] (a) N. A. Romero and D. A. Nicewicz, Chem. Rev., 2016, 116, 10075-10166; (b) Q. Liu and L. -Z. Wu, Natl. Sci. Rev., 2017, 4, 359-380.

[2] D. M. Schultz and T. P. Yoon, Science, 2014, 343, 1239176.

[3] (a) S. Rohe, A. O. Morris, T. McCallum, L. Barriault, Angew. Chem. Int. Ed. 2018, 57, 15664-15669; (b) H. P. Deng, Q. Zhou, J. Wu, Angew. Chem. Int. Ed. 2018, 57, 12661-12665.

[4] (a) H. P. Deng, X. Z. Fan, Z. H. Chen, Q. H. Xu, J. Wu, J. Am. Chem. Soc. 2017, 139, 13579-13584. (b) Y. Y. Loh, K. Nagao, A. J. Hoover, D. Hesk, N. R. Rivera, S. L. Colletti, I. W. Davies, D. W. C. MacMillan, Science 2017, 358, 1182-1187.

[5] (a) G. J. Choi, Q. L. Zhu, D. C. Miller, C. J. Gu, R. R. Knowles, Nature 2016, 539, 268-271. (b) C. M. Morton, Q. L. Zhu, H. Ripberger, L. Troian-Gautier, Z. S. D. Toa, R. R. Knowles, E. J. Alexanian, J. Am. Chem. Soc. 2019, 141, 13253-13260.

[6] Q. Q. Zhou, Y. Q. Zou, L. Q. Lu, W. J. Xiao, Angew. Chem. Int. Ed. 2019, 58, 1586-1604.

[7] J. Twilton, C. Le, P. Zhang, M. H. Shaw, R. W. Evans and D. W. C. MacMillan, Nat. Rev. Chem., 2017, 1, 0052.

[8] (a) J. C. Tellis, D. N. Primer and G. A. Molander, Science, 2014, 345, 433-436; (b) E. B. Corcoran, M. T. Pirnot, S. Lin, S. D. Dreher, D. A. DiRocco, I. W. Davies, S. L. Buchwald and D. W. C. MacMillan, Science, 2016, 353, 279-283; (c) Z. Dong and D. W. C. MacMillan, Nature, 2021, 598, 451-456; (d) A. L´opez-Magano, B. Ort´ın-Rubio, I. Imaz, D. Maspoch, J. Alem´an and R. Mas-Ballest´e, ACS Catal., 2021, 11, 12344-12354.

[9] Yu, J.; Zhao, C.; Zhou, R.; Gao, W.; Wang, S.; Liu, K.; Chen, S.; Hu, K.; Mei, L.; Yuan, L.; Chai, Z.; Hu, H.; Shi, W. Visible-Light-Enabled C-H Functionalization by a Direct Hydrogen Atom Transfer Uranyl Photocatalyst. Chem. Eur. J.; 2020, 26, 16521-16529.

[10] (a) F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klçck, M. OQKeeffe, O. M. Yaghi, J. Am. Chem. Soc. 2009, 131, 4570-4571; (b) T. Zhou, S. Xu, Q. Wen, Z. Pang, X. Zhao, J. Am. Chem. Soc. 2014, 136, 15885-15888; (c) C. Qian, Q. Qi, G. Jiang, F. Cui, Y. Tian, X. Zhao, J. Am. Chem. Soc. 2017, 139, 6736-6743. (d) Y. Zeng, R. Zou, Z. Luo, H. Zhang, X. Yao, X. Ma, R. Zou, Y. Zhao, J. Am. Chem. Soc. 2015, 137, 1020-1023.

[11] (a) T. Sick, A. G. Hufnagel, J. Kampmann, I. Kondofersky, M. Calik, J. M. Rotter, A. Evans, M. Dçblinger, S. Herbert, K. Peters, D. Bçhm, P. Knochel, D. D. Medina, D. Fattakhova-Rohlfing, T. Bein, J. Am. Chem. Soc. 2018, 140, 2085-2092; (b) V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, F. Podjaski, C. Ochsenfeld, B. V. Lotsch, Nat. Commun. 2015, 6, 8508; (c) L. Chen, K. Furukawa, J. Gao, A. Nagai, T. Nakamura, Y. Dong, D. Jiang, J. Am. Chem. Soc. 2014, 136, 9806-9809; (d) C. R. DeBlase, K. E. Silberstein, T. Truong, H. D. AbruÇa, W. R. Dichtel, J. Am. Chem. Soc. 2013, 135, 16821-16824; (e) S. Ding, M. Dong, Y. Wang, Y. Chen, H. Wang, C. Su, W. Wang, J. Am. Chem. Soc. 2016, 138, 3031-3037; (f) H. Xu, J. Gao, D. Jiang, Nat. Chem. 2015, 7, 905-912; (g) N. Huang, R. Krishna, D. Jiang, J. Am. Chem. Soc. 2015, 137, 7079-7082.

[12] (a) W. Guan, L. Zhou, Y. Dong, Chem. Soc. Rev., 2022, 51, 6307-6416.

[13] (a) W. Dong, Y. Yang, Y. Xiang, S. Wang, P. Wang, J. Hu, L. Rao and H. Chen, Green Chem., 2021, 23, 5797-5805; (b) H. Chen, W. Liu, A. Laemont, C. Krishnaraj, X. Feng, F. Rohman, M. Meledina, Q. Zhang, R. Van Deun, K. Leus and P. Van Der Voort, Angew. Chem., Int. Ed., 2021, 60, 10820-10827.

[14] Y.-N. Gong, W. Zhong, Y. Li, Y. Qiu, L. Zheng, J. Jiang and H.-L. Jiang, J. Am. Chem. Soc., 2020, 142, 16723-16731.